

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

220986US0PCT

10/089162

PRIORITY DATE CLAIMED  
27 September 1999

# PROCESS FOR TREATMENT AND EXTRACTION OF ORGANIC CORK COMPOUNDS BY A DENSE FLUID UNDER PRESSURE


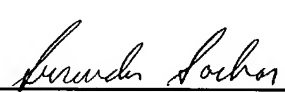
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☒ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

**Items 13 to 20 below concern document(s) or information included:**

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☐ Certificate of Mailing by Express Mail
23. ☒ Other items or information:

### Request for Consideration of Documents Cited in International Search Report

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.101) <b>10/089162</b>		INTERNATIONAL APPLICATION NO. <b>PCT/FR00/02653</b>		ATTORNEY'S DOCKET NUMBER <b>220986US0PCT</b>					
24. The following fees are submitted: <b>BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :</b> <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... <b>\$1040.00</b> <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... <b>\$890.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b> <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... <b>\$100.00</b> <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				<b>CALCULATIONS PTO USE ONLY</b>  <table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:50%;"><b>\$890.00</b></td> <td style="width:50%;"></td> </tr> <tr> <td><b>\$0.00</b></td> <td></td> </tr> </table>		<b>\$890.00</b>		<b>\$0.00</b>	
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Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td style="width:50%;"></td> <td style="width:50%;"></td> </tr> <tr> <td><b>\$0.00</b></td> <td></td> </tr> </table>				<b>\$0.00</b>	
<b>\$0.00</b>									
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE						
Total claims	30 - 20 =	10	x \$18.00	<b>\$180.00</b>					
Independent claims	3 - 3 =	0	x \$84.00	<b>\$0.00</b>					
Multiple Dependent Claims (check if applicable).				<input type="checkbox"/>	<b>\$0.00</b>				
<b>TOTAL OF ABOVE CALCULATIONS</b>				<b>=</b>	<b>\$1,070.00</b>				
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				<b>\$0.00</b>					
<b>SUBTOTAL</b>				<b>=</b>	<b>\$1,070.00</b>				
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				<b>\$0.00</b>					
<b>TOTAL NATIONAL FEE</b>				<b>=</b>	<b>\$1,070.00</b>				
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	<b>\$0.00</b>				
<b>TOTAL FEES ENCLOSED</b>				<b>=</b>	<b>\$1,070.00</b>				
				<b>Amount to be refunded</b>	<b>\$</b>				
				<b>charged</b>	<b>\$</b>				
a. <input checked="" type="checkbox"/> A check in the amount of <u><b>\$1,070.00</b></u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u><b>15-0030</b></u> A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. <b>WARNING:</b> Information on this form may become public. <b>Credit card information should not be included on this form.</b> Provide credit card information and authorization on PTO-2038.									
<b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.</b>									
<b>SEND ALL CORRESPONDENCE TO:</b> <div style="border: 1px solid black; padding: 10px; margin-top: 10px; display: inline-block;"> <b>Surinder Sachar</b>  <b>Registration No. 34,423</b>    <b>22850</b> </div>									
			<div style="text-align: right; margin-bottom: 10px;">           SIGNATURE       </div> <div style="text-align: right; margin-bottom: 10px;"> <b>Norman F. Oblon</b>          NAME       </div> <div style="text-align: right; margin-bottom: 10px;"> <b>24,618</b>          REGISTRATION NUMBER       </div> <div style="text-align: right;"> <u>March 27 2002</u>          DATE       </div>						

220986US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :

GUY LUMIA ET AL. :

SERIAL NO: NEW U.S. PCT APPLN. : ATTN: APPLICATION BRANCH  
(Based on PCT/FR00/02653)

FILED: HEREWITH :

FOR: PROCESS FOR TREATMENT AND  
EXTRACTION OF ORGANIC CORK  
COMPOUNDS BY A DENSE FLUID  
UNDER PRESSURE

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS  
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown on the marked-up copy following this amendment to read as follows.

3. (Amended) Process according to claim 1, in which said dense fluid under pressure is in the super-critical state.

4. (Amended) Process according to claim 1, in which compression/decompression cycles are carried out.

7. (Amended) Process according to claim 1, in which a co-solvent is added to the dense fluid under pressure.

10. (Amended) Process according to claim 7, in which said co-solvent is added to the dense fluid under pressure with a content of 0.01 to 10% by weight.

12. (Amended) Process for selective extraction of contaminating organic compounds from cork or a cork-based material, in which said material is treated by contacting said material with a dense fluid under pressure at a temperature of from 10 to 120°C and at a pressure of from 10 to 600 bars and adding a co-solvent to the dense fluid under pressure.

16. (Amended) Extraction process according to claim 12, in which the dense fluid under pressure is CO<sub>2</sub> and the co-solvent is water or an aqueous solution.

17. (Amended) Treatment or extraction process according to claim 1, in which the fluid and the extracts are separated by one or several steps, after the treatment or the extraction by the dense fluid under pressure, and the gaseous fluid is recycled.

18. (Amended) Process according to claim 1, in which said cork or said cork-based material is also subjected to a mechanical and/or chemical treatment before or after said treatment or said extraction by the dense fluid under pressure, and particularly treatment by hot or boiling water commonly called a "boiling treatment".

19. (Amended) Process according to claim 1, in which said cork or said cork-based material is shaped before or after said treatment or said extraction using the dense fluid under pressure; or earlier than said optional mechanical and/or chemical treatment, preceding said treatment or said extraction by the dense fluid under pressure; or later than said optional mechanical and/or chemical treatment, following said treatment or said extraction by the dense fluid under pressure.

21. (Amended) Manufacturing process for bottle corks made of cork or made of a cork-base material, comprising at least one treatment or extraction step according to claim 1.

22. (Amended) Manufacturing installation for parts made of cork or of a cork-based material such as bottle corks comprising a treatment or extraction installation by bringing said cork or said material into contact with a dense fluid under pressure under the conditions specified in claim 1, the said installation comprising: means of bringing the cork or a cork-based material into contact with a dense fluid under pressure in the form of an extractor or autoclave (1); means of circulating the fluid and bringing it to the dense state under pressure comprising a pump, a liquefier and a super-critical exchanger; separation means firstly for separating organic compounds extracted from said cork and said cork-based material in liquid form, and secondly the fluid in gaseous form; and means of recycling the fluid thus separated from the extractor by using the means of circulating the fluid and bringing it into the dense state and under pressure.

Please add the following new claims.

24. (New) Process according to claim 8, in which said co-solvent is added to the dense fluid under pressure with a content of 0.01 to 10% by weight.

25. (New) Treatment or extraction process according to claim 12, in which the fluid and the extracts are separated by one or several steps, after the treatment or the extraction by the dense fluid under pressure, and the gaseous fluid is recycled.

26. (New) Process according to claim 12, in which said cork or said cork-based material is also subjected to a mechanical and/or chemical treatment before or after said treatment or said extraction by the dense fluid under pressure, and particularly treatment by hot or boiling water commonly called a "boiling treatment".

27. (New) Process according to claim 12, in which said cork or said cork-based material is shaped before or after said treatment or said extraction using the dense fluid under pressure; or earlier than said optional mechanical and/or chemical treatment, preceding said treatment or said extraction by the dense fluid under pressure; or later than said optional mechanical and/or chemical treatment, following said treatment or said extraction by the dense fluid under pressure.

28. (New) Process according to claim 27, in which said cork or said cork-based material is put into the form of bottle corks, boards or sheets.

29. (New) Manufacturing process for bottle corks made of cork or made of a cork-base material, comprising at least one treatment or extraction step according to claim 12.

30. (New) Manufacturing installation for parts made of cork or of a cork-based material such as bottle corks comprising a treatment or extraction installation by bringing said cork or said material into contact with a dense fluid under pressure under the conditions specified in claim 12, the said installation comprising: means of bringing the cork or a cork-based material into contact with a dense fluid under pressure in the form of an extractor or autoclave (1); means of circulating the fluid and bringing it to the dense state under pressure comprising a pump, a liquefier and a super-critical exchanger; separation means firstly for separating organic compounds extracted from said cork and said cork-based material in liquid form, and secondly the fluid in gaseous form; and means of recycling the fluid thus separated from the extractor by using the means of circulating the fluid and bringing it into the dense state and under pressure.

REMARKS

Claims 1-30 are active in the present application. Claims 1-23 have been amended to remove multiple dependencies. Claims 19 has been amended for clarity. Claim 22 has been amended to further describe the manufacturing installation. Support for amended Claim 22 is found on page 27, line 12 through page 31, line 16. Claims 24-30 are new claims. Support for the new claims is found in the original claims. No new matter is added. An action on the merits and allowance of claims is solicited.

Respectfully submitted,

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MAIER & NEUSTADT, P.C.



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<b>Marked-Up Copy</b> Serial No: <hr/> Amendment Filed on: <u>3-27-2002</u>
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IN THE CLAIMS

Please amend the claims as follows.

--3. (Amended) Process according to [either of claims 1 and 2] claim 1, in which said dense fluid under pressure is in the super-critical state.

4. (Amended) Process according to [any one of claims 1 and 3] claim 1, in which compression/decompression cycles are carried out.

7. (Amended) Process according to [any one of claims 1 to 6] claim 1, in which a co-solvent is added to the dense fluid under pressure.

10. (Amended) Process according to [any one of claims 7 to 8] claim 7, in which said co-solvent is added to the dense fluid under pressure with a content of 0.01 to 10% by weight.

12. (Amended) Process for selective extraction of contaminating organic compounds from cork or a cork-based material, in which said material is treated by [the process according to any one of claims 7 to 11] contacting said material with a dense fluid under pressure at a temperature of from 10 to 120°C and at a pressure of from 10 to 600 bars and adding a co-solvent to the dense fluid under pressure.



16. (Amended) Extraction process according to [any one of claims 12 to 15] claim 12, in which the dense fluid under pressure is CO<sub>2</sub> and the co-solvent is water or an aqueous solution.

17. (Amended) Treatment or extraction process according to [any one of claims 1 to 16] claim 1, in which the fluid and the extracts are separated by one or several steps, after the treatment or the extraction by the dense fluid under pressure, and the gaseous fluid is recycled.

18. (Amended) Process according to [any one of claims 1 to 17] claim 1, in which said cork or said cork-based material is also subjected to a mechanical and/or chemical treatment before or after said treatment or said extraction by the dense fluid under pressure, and particularly treatment by hot or boiling water commonly called a "boiling treatment".

19. (Amended) Process according to [any one of claims 1 to 18] claim 1, in which said cork or said cork-based material is shaped before or after said treatment or said extraction using the dense fluid under pressure; [either] or earlier than said optional mechanical and/or chemical treatment, [if any,] preceding said treatment or said extraction by the dense fluid under pressure; or later than said optional mechanical and/or chemical treatment, [[if any, after] following said treatment or said extraction by the dense fluid under pressure.

21. (Amended) Manufacturing process for bottle corks made of cork or made of a cork-base material, comprising at least one treatment or extraction step according to [any one of claims 1 to 18] claim 1.

22. (Amended) Manufacturing installation for parts made of cork or of a cork-based material such as bottle corks comprising a treatment or extraction installation by bringing said cork or said material into contact with a dense fluid under pressure under the conditions

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PROCESS FOR TREATMENT AND EXTRACTION OF ORGANIC CORK  
COMPOUNDS BY A DENSE FLUID UNDER PRESSURE

This invention relates to a process for the treatment and extraction of organic cork compounds using a dense fluid under pressure, and particularly a super-critical fluid.

5 Cork is a natural impermeable and lightweight material derived from the bark of some types of oak such as cork oak, most of which are found in countries bordering the Mediterranean, in Europe and in North Africa.

10 Cork is used particularly for making bottle corks used to close receptacles such as bottles containing liquids for food consumption, particularly wine.

Bottle corks have been used to close wine bottles for very many years.

15 About 15 billion bottles are closed in this manner throughout the world every year.

Cork is a natural product that has properties particularly well suited for conserving wine in bottles. Cork is elastic, resilient, compressible, has  
20 a high coefficient of friction, is impermeable to liquids, and has a sufficient permeability to gases to enable the exchanges necessary for the product to mature in bottles.

However, occasionally, some alterations to the  
25 smell and/or taste of the conserved liquid such as wine compromise the coherence of the natural pair consisting of the cork and the wine.

These alterations are all referred to under the generic term "corky flavour".

It has been shown that most of these alterations are completely independent of the cork (stopper) and  
5 originate in the wine itself or in its preparation and storage.

However, other alterations are caused by the cork (stopper) and a great deal of work has been done throughout the world to find the cause of the problem  
10 and to find a solution.

Thus, it has been found that cork tastes can be globally distributed into "genuine" corky flavours, corky flavours, and finally musty tastes.

A "genuine" corky flavour is a putrid taste making  
15 the wine undrinkable. This defect is related to yellow stain, in other words growth of a higher fungus, *Armillaria mellea*.

Cork boards affected by yellow stain are usually put aside during the first cork board selection sort.

20 The frequency of this defect is of the order of 1 in 10 000 to 1 in 100 000.

The corky flavour is due to the fact that cork is not inert towards wine. It provides aromatic compounds in variable proportions that can interact positively or  
25 negatively with the wine.

The presence of more or less accentuated undesirable tastes is related to preparation of cork, particularly the storage duration in the yard and boiling conditions.

30 The frequency at which these tastes occur can be minimised by respecting the *Code International des*

*Pratiques Bouchonnières* (International Cork-cutter Practices Code).

A "corky flavour" and a "musty taste" are very often confused. Musty tastes are fungus, forest  
5 undergrowth and mould type tastes related to the presence of organic molecules, the most frequently mentioned being methyl-isoborneol and its derivatives with a "musty and camphrous" smell, geosmine with an  
"earthy" smell, methylthio-ethyl-pyrazine with a "musty  
10 and sulphurous" smell, alcohols and unsaturated cetones in  $C_8$  with a "mushroomy" smell, and particularly chloroanisoles and especially 2,3,4,6-TeCA, 2,4,6-TCA (trichloroanisole) and 2,3,4,6-TeCA (tetrachloro-anisole).

15 These chloroanisoles, which smell very strongly and for which the perception threshold in water is between 0.03 and 4 ng/l, originate from methylation of slightly volatile chlorophenols that have a very mild smell. This reaction is carried out by a very large  
20 number of moulds and is equivalent to a chlorophenol detoxification reaction.

Chlorophenol type precursors may originate from different locations and from health care products, insecticide treatments, atmospheric pollution and cork  
25 degradation reactions, for example subsequent to some washing operations by hypochlorite.

Finally, particularly to eliminate "corky flavours" as much as possible, cork is subjected to various treatments and particularly cleaning  
30 operations.

Cleaning treatments and operations take place at different stages in the production or maintenance of cork objects, for example such as bottle corks (stoppers).

5       A treatment consists of eliminating micro-organisms from the cork, responsible for the production of undesirable metabolites during the treatments themselves after finishing.

10       Thus, before the bottle corks are finished, they are washed with chlorine using lime chloride or hypochlorite followed by washing with oxalic acid using a traditional process, or washing with peroxide (hydrogen peroxide or peracetic acid), or using sulfamic acid, or they are washed with metabisulfite  
15       using a solution of  $\text{SO}_2$ .

After the bottle corks have been finished (washed or unwashed), they are treated by the injection of  $\text{SO}_2$ , by ethylene oxide or by gamma radiation.

20       The most frequently used process for eliminating volatile compounds responsible for tastes is the use of hot or boiling water, known as "boiling".

25       Thus, in the F. BORDAS process that was first used in 1904, the parts are placed in a chamber heated to  $120^\circ\text{C}$  for 10 minutes and a vacuum is then created, and then the pressure is restored by allowing steam to  
penetrate.

The chamber is then heated to  $130^\circ\text{C}$  for 10 minutes.

30       This old method has never been supported by any precise and evaluated data.

The CHAMPCORK process consists of putting parts in a chamber saturated with steam at 130°C and a pressure of 180 kPa for 18 - 20 minutes. Atmospheric pressure is then restored.

5 All these techniques described above have many disadvantages, including:

- low efficiency towards organic compounds causing undesirable tastes;
  - incomplete efficiency towards some micro-
- 10 organisms.

Furthermore, most of the techniques mentioned use chemical products that introduce risks, nuisances and constraints, both for the personnel who are using them and for the environment.

15 Thus, operators are exposed to the risk of inhaling noxious substances, which makes it necessary to wear a mask, whereas the effluents generated by these treatments contain large quantities of compounds containing sulphur and/or chlorine and must be  
20 subjected to a long and expensive purification process before they can be rejected.

The document by MIRANDA, Ana M. et al, "High-pressure extraction of cork with CO<sub>2</sub> and 1,4 dioxane", Process. Technol. Proc. (1996), 12 (High Pressure  
25 Chemical Engineering), pages 417 - 422, discloses a process for the treatment of cork using high pressure mixes (170 bars) of CO<sub>2</sub> and dioxane within a temperature range from 160°C to 180°C. Suberine is extracted in this manner.

30 The conditions of the process disclosed in this document are completely incompatible with use of cork

Document US-A-5 364 475 discloses a wood cleaning process, particularly a process for extraction of pentachlorophenol (PCP) type compounds or other non-ionic biocide organic compounds in which the wood is firstly cut into suitable size pieces, and is then subjected to a treatment by a fluid in the supercritical state, for example CO<sub>2</sub>.

The process according to this document is only applicable to pentachlorophenol (trichloroanisoie and tetrachloroanisoie are excluded) and can only extract contents compatible with potential changes to some environmentalist standards (Toxicity Characteristic Leaching Profile Level) (of the order of 0.1 ppm).

30 Furthermore, this patent states that the treated product must be divided into particles with a thickness



5 This grinding and shredding step is extremely penalising and it means that the process cannot be used to treat cork boards or bottle corks under any circumstances.

A co-solvent such as ethanol or isopropanol can be added to the super-critical fluid with a content of 2 to 5% by volume of the moisture content in the wood.

The extracted polluting organic compounds are particularly polychlorobiphenyls, chlorophenols and polychlorophenols (PCP), lindane, polyaromatic organic compounds, insecticides, fungicides, and other additives that might be found in the wood.

**B 13335.3 PA**

None of the processes described above using a dense fluid under pressure is applied to cork, but cork is an extremely specific material for which the properties are very different from the properties of wood, mainly in terms of elasticity and density.

It could be added that the chemical composition of cork is very different from the chemical composition of wood, particularly concerning the composition in suberine, lignin and cellulose.

The chemical composition of cork is usually as follows:

46% suberine (the main constituent of cork). The very high compressibility and elasticity of cork are due to the presence of large quantities of suberine.

25% lignin (structure of the cellular walls).

12% cellulose and other polysaccharides. Cork cellulose is in free form.

6% tannins.

6% ceroids. Ceroids repel water and contribute to the impermeability of cork.

5% ash and other compounds.

Refer to the following documents for further information on this subject:

A. Guillemonat. *Progrès récents dans l'étude de la constitution chimique du liège* (Recent progress in the study of the chemical composition of cork). Ann. Fac. Sc. De Marseille, 1960, 30, 43-54.

H. Pereira. Chemical composition and variability of cork from *Quercus suber* L. wood Sci. Technol., 1988, 22 (3), 211-218.

The chemical composition of dry wood is usually as follows, for comparison purposes:

60% cellulose.

25% lignin (structure of cellular walls).

5 15% other compounds.

Cork is a specific material and is fundamentally different from wood due to this difference in its composition.

10 The study of prior art described above shows that there is a need that has not been satisfied for a process for the treatment or cleaning of cork in order to eliminate contaminating and polluting organic compounds such as chlorophenols and chloroanisoles responsible particularly for undesirable tastes and  
15 smells.

There is still a need for a process for cleaning cork in order to selectively eliminate the said contaminating organic products without also affecting some other organic compounds such as suberine, ceroids,  
20 lignin and cellulose that confer desirable or even essential properties to the cork, particularly in view of its use for the manufacture of bottle corks.

Preferably, this process must also simultaneously eliminate or limit the presence and proliferation of  
25 micro-organisms such as bacteria and fungi in cork.

The purpose of this invention is to provide a cork treatment process that satisfies a number of requirements including all the needs and requirements mentioned above.

30 Another purpose of this invention is to provide a process for the treatment of cork that does not have

the defects, disadvantages, limitations and disadvantages of processes according to prior art and that solves problems with processes according to prior art.

5 This purpose and other purposes are achieved according to the invention by a process for the treatment of cork or a cork-based material in which the cork or the said cork-based material is put into contact with a dense fluid under pressure at a  
10 temperature of from 10 to 120°C and at a pressure of from 10 to 600 bars.

"Cork" refers to materials made exclusively of cork, while cork-based material treated by the process according to the invention refers to materials usually  
15 containing a high proportion of cork, composite cork-based materials, etc.

As we will see later, cork or the cork-based material may be shaped or unshaped.

Under the temperature and pressure conditions of  
20 the process according to the invention, cork or the cork-based material can be cleaned and/or decontaminated with an excellent efficiency.

In other words, with the process according to the invention, it is possible to extract and / or eliminate  
25 all or almost all contaminants, pollutants and undesirable or organic compounds located in cork or the cork-based material, without affecting the content of compounds naturally present in cork or the cork-based material such as ceroids, suberine, lignin and  
30 cellulose, or keeping them at an acceptable level.

These compounds and their contents confer the necessary and essential properties to cork for most of its applications, and particularly for the manufacture of bottle corks.

5           Therefore, the properties of cork related to these compounds and their contents, are not deteriorated by the treatment in the process according to the invention.

10           In particular, these properties are physical, chemical and organoleptic.

          The process according to the invention can be used to obtain cork or a cork-based material for which the properties after treatment are excellent, and are equivalent to or better than the properties of cork or  
15   the cork-based material treated by processes according to prior art, without any of their disadvantages.

          Thus, and as already mentioned above, due to the drastic temperature and pressure conditions involved, the process disclosed in the document by MIRANDA et al.  
20   causes a considerable deterioration of the properties of cork, such that they become completely incompatible with use of cork after this treatment for the manufacture of bottle corks. Furthermore, the purpose of this document is fundamentally different, since  
25   unlike the process according to the invention, the objective is to extract suberine from cork, and not to keep the suberine in cork in order to preserve its properties.

          Similarly, the process disclosed in this document  
30   is not intended to extract or specifically eliminate

undesirable organic compounds, which is the essential purpose of this invention.

According to the invention, use of the fluid in the dense state under pressure under the conditions  
5 defined above can advantageously replace and / or improve conventional cork cleaning and / or decontamination processes.

According to the invention, the fluid in the dense state under pressure is preferably put into contact  
10 with cork or the cork-based material at a pressure of 100 to 300 bars and at a temperature of 40 to 80°C.

Also preferably, the said dense fluid under pressure is a fluid in the super-critical state, in other words the dense fluid is at a pressure and under  
15 a temperature such that the fluid is in the super-critical state.

Thus, in the process according to the invention, a gaseous compound for example is used under normal temperature and pressure conditions, and its density is  
20 increased by increasing its pressure. The temperature can also be modified to enter the range in which the fluid is in the dense state and under pressure, preferably in its super-critical state. Those skilled in the art will find it easy to define this range.

25 According to the invention, the extractive properties of the fluid can be varied in a controlled manner by varying the pressure and the temperature parameters while remaining within the dense range under pressure, and preferably within the super-critical  
30 range for the fluid concerned; thus, increasing the pressure and temperature increases the solubilisation

capacity, whereas reducing the pressure reduces the viscosity and increases the diffusivity.

Thus, according to the invention, during the treatment it is possible to carry out  
5 compression/decompression cycles, preferably very fast cycles for example with an amplitude of the pressure variation from 10 to 100 bars and time intervals varying from ten seconds to a few minutes, for example 10 minutes, the complete process continuing for example  
10 for between 1 and several hours, for example 10 hours.

This increases the penetration of the solvent fluid into the material, which has the result of improving the cleaning performances and the internal flexibility of the cork.

15 The advantages of the process according to the invention are essentially related to the specific characteristics of fluids in the dense state under pressure, and particularly in the super-critical state, and due to the fact that, surprisingly, this technique  
20 can be applied to cork.

Considering the considerable differences between the properties of wood and cork, it was absolutely unpredictable that a process similar to the process for treating wood could also be applicable to cork or to  
25 cork-based materials.

The difference in composition between wood and cork that was clearly demonstrated above means that cork is an extremely specific material and that application of a dense fluid under pressure to treat  
30 cork could not be deduced from use of the same fluid to treat wood. Furthermore, the process according to the





The relative chemical inertia of CO<sub>2</sub> in the dense state makes it particularly suitable for use in a process designed to clean cork or a cork-based material, particularly when this cork or this material  
5 is intended to be used to make parts for food applications such as bottle corks.

Furthermore, the low viscosity of CO<sub>2</sub> in the dense state, its high diffusion coefficients and its very low interface tension enable cleaning of cork parts with  
10 complex shapes and complex physical characteristics, particularly in the presence of adsorption phenomena, either on the surface of the part or internally.

The advantages of CO<sub>2</sub> also include the fact that it can be used as a complement to or as a replacement  
15 for conventionally used processes:

- an almost perfect extraction efficiency for undesirable organic compounds, due to specific physicochemical characteristics;
- an almost zero residual effluent volume,  
20 limited strictly to recuperation of extracted pollutants (including PCP and TCA) and recycling of purified CO<sub>2</sub> gas;
- a large saving, for example in terms of solvent due to the lack of treatment or recuperation of  
25 effluents, or due to the use of inexpensive CO<sub>2</sub>;
- respect of the environment, since the process generates no or very few aqueous effluents;
- modularity of the dissolving capacity of the molecule that varies as a function of usage conditions,  
30 in other words the pressure and the temperature, in

order to adapt to the nature of the products to be extracted and / or the required application.

In other words, the pressure and temperature characteristics can be used to control a fluid for which the dissolving capacity can be varied in terms of solubilisation, and particularly contaminating, polluting and undesirable compounds of cork, and the extraction dynamics particularly within the porous solid matrix from which the cork is formed.

The excellent volatility of  $\text{CO}_2$  under normal conditions (temperature and pressure) characterises it as a dry solvent not requiring any drying step after cleaning. Furthermore,  $\text{CO}_2$  does not leave any residual trace on the treated part.

Treatment in a  $\text{CO}_2$  atmosphere can avoid risks of oxidation and improve the final surface condition of the part.

Preferably, according to the invention, a "co-solvent" compound is added to the dense fluid under pressure. The addition of this type of co-solvent to a dense fluid under pressure within the specific context of treatment of cork, is not described or even suggested in prior art.

Surprisingly, according to the invention, it was observed that the addition of a co-solvent to the dense fluid under pressure can result in total extraction of contaminating and polluting organic compounds, in other words undesirable compounds, from cork or a cork-based material.

As mentioned above, the addition of the co-solvent guarantees selective extraction of undesirable organic

compounds, while maintaining acceptable levels of the content of compounds naturally present in the cork such as ceroids, suberine, lignin and cellulose.

In other words, the addition of an appropriate co-solvent is a means of controlling the selectivity towards the extraction of pollutants, contaminants and undesirable organic compounds that are to be eliminated and extracted.

Furthermore, and completely surprisingly, it has been observed that the addition of a co-solvent causes a reduction in the growth of micro-organisms very much greater than the reduction obtained with CO<sub>2</sub> alone, due to a type of synergy effect, and this reduction in the growth of micro-organisms can change from a factor of 100 to a factor of 1 million when the co-solvent is added.

According to the invention, the said co-solvent is chosen for example from among water, aqueous solutions, alcohols, for example aliphatic alcohols from 1 to 5 C such as ethanol, methanol, butanol, cetones such as acetone, and their mixtures.

Among aqueous solutions, it is worth mentioning buffer solutions for example such as phosphate and/or hydrogenosphosphate solutions, etc., to stabilise the pH of the process; antibiotic solutions such as penicillin and / or fungicide solutions, to increase the elimination of micro-organisms; anti-oxidant solutions such as ascorbic acid to stabilise the material, etc.

According to the invention, the said co-solvent is added to the dense fluid under pressure with a content

of 0.01 to 10% by weight, and preferably 0.02 to 1% by weight and even more preferably 0.02 to 0.1% by weight.

If the co-solvent is water, part of it may already be present in cork, and only the necessary quantity to  
5 give the concentrations mentioned above will be added to the super-critical fluid.

Thus, the invention also relates to a process for selective extraction of contaminating organic compounds from cork or a cork-based material, in which the said  
10 cork-based material is treated by bringing it into contact with a dense fluid under pressure under the temperature and pressure conditions according to the invention, a co-solvent being added to the dense fluid under pressure.

15 The contaminating or polluting organic compounds mentioned above, to which the process according to the invention can be applied, are organic compounds that could be located in cork and that form pollutants or contaminants that must be eliminated to enable use of  
20 cork or the cork-based material without any disadvantages.

Other organo-chlorinated compounds such as lindane and polyaromatic organic compounds (HPA) may also be extracted using the process according to the invention.

25 The process according to the invention is also applicable to the extraction of organic compounds such as triazole, synthetic pyrethroids, insecticides and fungicides that may be present in cork.

Note that for simplification reasons, the term  
30 "organic compounds" is frequently used in the plural in the description, although it is obvious that the

process according to the invention may apply to a single organic compound.

According to the invention, the said extracted contaminating, polluting organic compounds are  
5 essentially and preferably the organic compounds responsible for undesirable tastes and/or smells.

An "undesirable" taste or smell usually means a taste or a smell that is not required in cork, particularly under the conditions under which it is  
10 used, for example when coming into contact with a consumable liquid.

An "undesirable" taste or smell can generally be defined as a taste or smell considered to be "unpleasant" by most users.

15 These compounds responsible for undesirable tastes and / or smells are usually (poly)chlorophenols and other phenolic compounds and (poly)chloroanisoles and other derivatives of anisole, and particularly pentachlorophenol (PCP), trichloroanisole (TCA) and  
20 tetrachloroanisole (TeCA).

The compounds mentioned above are present in cork either naturally or in an induced manner.

Extraction according to the process described in our patent is done on organic products that do not  
25 originate from a treatment carried out intentionally as is the case for cut wood (trunks, boards, etc.) for preservation of boards or other wood-based materials that need to be depolluted for recycling purposes.

As already mentioned above, surprisingly the  
30 extraction process according to the invention can be used for complete and selective elimination of organic

compounds responsible for undesirable tastes and / or  
smells in cork, while keeping the content of a number  
of compounds such as ceroids, suberine, tannins, lignin  
and cellulose conferring physical, chemical and  
5 organoleptic and mechanical qualities essential to  
cork, particularly when it is used for the production  
of bottle corks, at a suitable level.

The elimination of undesirable organic compounds  
and particularly TCA, without simultaneously  
10 eliminating ceroids necessary particularly for the good  
mechanical behaviour of a bottle cork, is a surprising  
effect of the process according to the invention and is  
not described or suggested by prior art.

The process thus satisfies a need that has not  
15 been satisfied for a long time in the state of the art  
and overcomes a widespread preconception among  
professionals in the cork business by which it is  
impossible to selectively eliminate undesirable  
compounds without affecting beneficial compounds.

20 Within the context of the extraction process  
according to the invention, the fluid used is  
preferably CO<sub>2</sub> and the co-solvent, chosen from among  
water and aqueous solutions is added to the CO<sub>2</sub> under  
pressure with a content of 0.01% to 10% by weight.

25 According to the invention, a selective extraction  
of pollutants and contaminants can be achieved together  
with a reduction (by synergy) of the growth of micro-  
organisms at contents of the co-solvent as low as 0.01%  
by weight, for example 0.02 to 1% by weight, and  
30 preferably 0.02 to 0.2% by weight.

The temperature and pressure ranges involved during the extraction or treatment operation can vary, provided that the fluid always remains a dense fluid under pressure, preferably in a super-critical state, and that compression / decompression cycles can also be carried out, as mentioned above.

The temperature and pressure ranges depend particularly on the nature of the fluid used.

These temperature and pressure ranges have already been mentioned above and are particularly applicable to CO<sub>2</sub>.

These conditions can be maintained throughout the duration of the process, or simply at the beginning of the extraction or treatment process, in which these conditions correspond to a high density and a high temperature - the overriding phenomenon being solubilisation - in order to very quickly extract compounds outside the matrix.

In general, the treatment or extraction time (in other words the time during which cork or the cork-based material is left in contact with the dense fluid under pressure) is between one or a few minutes, for example 10 minutes, or one or a few hours, for example 10 hours, depending on the fluid flow and the quantity of materials to be treated.

After a few minutes, in other words for example after 5 to 20 minutes, and when the pressure and temperature conditions according to the process are applied to the materials, the extraction takes place very quickly due to a very high diffusion capacity.

After reaching equilibrium, for example after 30 to 60 minutes, it can be considered that extraction is complete with an efficiency for example close to 99.9%.

Extraction efficiencies are always very high, even  
5 for compounds containing chlorine, for which the efficiency is better than 85%, for example 98%.

The solvent content used, in other words the weight of the dense fluid - solvent - preferably super-critical, used compared with the weight of cork or the  
10 cork-based material, is usually 10 to 100 kg of fluid / kg of cork or cork-based material.

Advantageously, the process according to the invention comprises a fluid recycling step after the extraction or treatment and after one or several  
15 physicochemical separation steps, in order to separate the fluid from the extracts.

Conventionally, the first separation steps consist of reducing the density of the fluid by a series of pressure reductions and temperature increases in order  
20 to get closer to the gaseous state.

The dissolving capacity of the fluid drops, and thus some of the extracts solubilised in the extraction step are recovered.

Thus, the process according to the invention for  
25 the extraction or treatment of cork can be used to physically separate the useable cork or the cork-based material usually representing about 90 to 99% of the initial product, from undesirable, natural or artificial organic products representing less than  
30 about 1% to 10% of the initial product and that can be manipulated, treated and eliminated specifically and



therefore can be easily controlled, while the gas or fluid may advantageously be recycled so that it can be used for another extraction or another treatment.

Consequently, the treatment or extraction process  
5 may be done in a closed circuit or in a loop which means that advantageously, due to an initial and constant content of a fluid such as  $\text{CO}_2$ , the undesirable organic compounds can be gradually depleted from the or the cork-based material.

10 More precisely and after the extraction process itself, the process according to the invention advantageously comprises one or several steps, for example up to three physicochemical separation steps in which the density of the fluid is reduced, for example  
15 by a series of pressure reductions and temperature increases, preferably between 1 and 3, in order to get closer to the gaseous state.

For example, the conditions in these successive steps may be 90 bars and  $50^\circ\text{C}$ , 70 bars and  $40^\circ\text{C}$ , 50  
20 bars and  $40^\circ\text{C}$ .

Since the isolating capacity of the fluid is reduced, the extracts previously solubilised in the extraction step are thus recovered.

These extracts are in the form of more or less  
25 fluid concentrated liquids and may be treated specifically and possibly destroyed in the case of pollutants.

The gas obtained at the end of the separation step is preferably recycled to the extraction step, where it  
30 is reconditioned in order to restore temperature and pressure conditions so that it is in a super-critical

state, the gas can thus be firstly cooled to atmospheric pressure, stored in liquid form and then heated and compressed before being sent to the extraction process itself.

5 Before being recycled, the gas is preferably purified, for example by active carbon, in order to eliminate traces of volatile organic products that were not separated in the previous step.

Thorough purification of the gas is usually  
10 necessary, otherwise extraction performances will be very much reduced.

According to the invention, cork or the cork-based material may also be subjected to a mechanical and / or chemical treatment, before the treatment or extraction  
15 using the dense fluid under pressure.

A mechanical and / or chemical treatment usually means a known treatment as described above within the context of the presentation of prior art.

This treatment is preferably a treatment using hot  
20 or boiling water, usually called a "boiling" treatment.

According to the invention, cork or the cork-based material is shaped before or after the said treatment or the said extraction using the dense fluid under pressure; either earlier than the said mechanical  
25 and / or chemical treatment, if any, preceding the said treatment or the said extraction by the dense fluid under pressure; or later than the said mechanical and / or chemical treatment, if any, after the said treatment or the said extraction by the dense fluid  
30 under pressure.

In other words, in the process according to the invention, the part or parts to be cleaned, in other words the unprocessed parts before or after stamping and before or after the mechanical and / or chemical  
5 treatment, and preferably the boiling treatment, are put into contact with the fluid in the dense state under pressure.

This shaping, working or stamping is intended to bring cork or the cork-based material, usually pure  
10 cork, into the shape required for the planned use, which may be boards, stamped or moulded bottle corks, for example bottle corks made of composite materials, cork parts used for the manufacture of objects or devices made for food or non-food applications.

15 We saw above that the process according to the invention is particularly suitable for preparing cork or a cork-based material with optimum qualities for manufacturing a bottle cork.

Thus, the invention also applies to a process for  
20 manufacturing bottle corks made of cork or made of a cork-based material, that includes at least one treatment or extraction step as described above.

The invention also relates to an installation for manufacturing parts such as bottle corks made of cork  
25 or made of a cork-based material, that includes an installation for the treatment or extraction of the said material by bringing it into contact with a dense fluid under pressure, under the conditions described above.

30 This step may be included at any point in the process for manufacturing bottle corks.

"Substantially free from" means that the content of these compounds is such that the undesirable smell and / or taste caused by the compounds is /are not present in cork or the cork-based material according to  
5 the invention.

Bottle corks according to the invention are particularly useful for closing off receptacles such as bottles, barrels, drums or other receptacles containing food products and preferably liquids such as wine  
10 products.

Finally, the invention relates to a process for disinfection of cork or cork-based material and / or making it aseptic by bringing the said material into contact with a dense fluid under pressure, to which a  
15 co-solvent is added.

The invention will be better understood after reading the following description with reference to the attached drawings, in which:

- figure 1 diagrammatically shows a sectional  
20 view of an elevation of an example installation for an embodiment of the process according to the invention;
- figure 2 is a graph showing the cleaning efficiency E as a percentage of cork parts with PCP and TCA supplements, boiled (at right) and unboiled (at  
25 left) for different treatment times t (in hours) and different densities of CO<sub>2</sub> (in g/l), the columns with close cross-hatching being applicable to PCP (pentachlorophenol) and columns with wide cross-hatching being applicable to TCA (2,4,6-  
30 trichloroanisole);

- figure 3 contains a graph showing the evaluation of the mechanical strength of "tubed" bottle corks cut from cork boards treated and not treated by CO<sub>2</sub>, and boiled and unboiled control parts;

5       The mechanical strength was evaluated by measuring compression pressures (PC) and return pressures (Pret).

- Figure 4 is a graph showing the logarithmic variation, variation (log), of microbial growth as a function of the applied temperature (T (°C)) during the  
10   treatment by CO<sub>2</sub> only (curve in dashed lines) or by CO<sub>2</sub> plus water (curve with solid lines).

Figure 1 diagrammatically shows a sectional view of an elevation of the installation according to the invention.

15       Obviously, a figure of this type only shows an example embodiment of an installation and is only given for illustrative purposes and are in no way restrictive.

This figure shows means of bringing the cork or  
20   cork-based material into contact in the form of an extractor or autoclave (1).

This type of extractor can resist the pressure applied in the process according to the invention and it is also provided with heating and temperature  
25   regulation means in the form of a thermostat controlled double shell (2), inside which a suitable heat transporting fluid (3), (4) can circulate.

The volume of the extractor or autoclave is variable, and depends particularly on the quantity of  
30   cork to be processed; it can easily be determined by those skilled in the art.

The cork or cork-based material parts to be treated (5), for example in the form of boards, sheets or bottle corks, are put into the extractor, and these parts are preferably placed on one or several supports  
5 or grills.

Figure 1 shows only one extractor (1) in the installation, but it is quite obvious that the installation may comprise several extractors (for example 2 to 10 laid out for example in series).

10 The installation also comprises means of bringing a fluid, such as CO<sub>2</sub> to the dense state under pressure, for example to the super-critical state.

Thus in figure 1, the fluid, for example CO<sub>2</sub>, from a recycling pipe (6) and / or possibly a storage and  
15 make up reservoir, for example CO<sub>2</sub> (7) penetrates through a valve (8) into a liquefaction reservoir (9) provided with temperature regulation means in the form of a thermostat controlled double shell (10), inside which a suitable heat transporting fluid (11, 12) can  
20 circulate.

The said fluid such as CO<sub>2</sub> is thus liquefied and circulates through a flowmeter (13), and is then pumped and compressed by a pump (14), for example a membrane type or piston type compression pump, or for example by  
25 a compressor to the extractor (1).

Before being introduced into the extractor (1) through a valve (15), the fluid, for example pumped CO<sub>2</sub>, is heated in an exchanger (16) called a "super-critical" exchanger in which it is heated until it is  
30 under conditions in which it is in the form of a dense

fluid under pressure, and in particular a dense super-critical fluid.

In other words, the fluid is heated above its critical temperature in this exchanger, which for  
5 example is 31.1°C for CO<sub>2</sub>.

Figure 1 also shows means of injecting a co-solvent in the form of a high pressure pump (17) supplied by a co-solvent reservoir (18) that progressively adds a known quantity of co-solvent in  
10 the compressed fluid through a pipe (19) connected to the fluid supply pipe to the extractor (1), on the input side of the exchanger (16) and on the output side of the compression pump (14).

Therefore, the temperature of the mix consisting  
15 of the compressed fluid and the co-solvent is increased to the working temperature through the exchanger (16).

According to the invention, the fluid and co-solvent mix impregnates the parts to be treated (5) made of cork or cork-based material, for example cork  
20 boards or bottle corks already stamped, in the chamber of the extractor (1), and extracts the undesirable contaminating chemical compounds.

One or several parts may be treated simultaneously, depending on the size of the parts to  
25 be treated.

The impurities contained in the fluid such as CO<sub>2</sub> will increase as a function of the contact time between the two bodies, provided that the solubility is not too great, by splashing.

Thus, the super-critical fluid at the inlet to the extraction autoclave (1) will be a homogeneous fluid solution such as CO<sub>2</sub> and co-solvent.

5 The cork content could also be mixed with a known proportion of co-solvent before the extraction operation, in other words before the fluid is added into the autoclave.

The current of fluid such as CO<sub>2</sub>, in which compounds extracted from the cork are solubilised, is  
10 then sent to separation means connected to the top of the extractor or the autoclave (1), and for example comprising three cyclone type separators (20, 21, 22) connected in series, each of them being preceded by an automatic pressure reduction valve (23, 24, 25).

15 Three cyclone type separators (20, 21, 22) are shown in figure 1, but it is obvious that the number, type and sequence of the separators can vary.

The pressure reduction applied to the fluid takes place at constant temperature.

20 The organic compounds in liquid form extracted from cork are separated or demixed from a gas, for example CO<sub>2</sub>, in each separator.

Compounds extracted from cork are drawn off (26, 27, 28), for example at the bottom of the separators,  
25 and are recovered and then other separation, extraction or purification operations, for example centrifuging, settlement or liquid / liquid extraction are possibly carried out on them, or they may be destroyed.

The gas derived from the separation, such as CO<sub>2</sub>,  
30 is cleaned and is then sent to fluid recycling means that comprise essentially a pipe (6) and a "cold"



exchanger (26) or liquefier, for example in the form of a thermostat controlled chamber, to be sent to the low temperature liquid reserve (9) kept cool by a cooling batch that cools and liquefies the fluid (11, 12) such  
5 as CO<sub>2</sub>.

The cleaning means (29) have been shown in figure 1 as a reflux column or an active carbon column (29) placed on the fluid recycling means.

Finally, the installation comprises regulation  
10 means (not shown), particularly for the pressure, in the different parts of the process, that comprise a regulation system composed of pressure sensors, regulators and pneumatically controlled needle valves.

The invention will now be described with reference  
15 to the following examples that are given for illustrative purposes and are in no way restrictive.

#### Examples

Cork samples were treated or cleaned using the  
20 process according to the invention, using an installation similar to that shown in figure 1, the fluid being dense CO<sub>2</sub> under pressure.

More precisely, this installation comprises:

- a CO<sub>2</sub> reserve in the form of a sphere  
25 containing about 300 kg, this type of sphere being commercially available;
- a liquefier in the form of a steel chamber occupying about 2 litres and with a low temperature thermostat control, by means of a cooling bath;
- 30 - a 0 to 300 bar compression pump with a maximum flow of 10 kg/h;

- a 0 to 300 bar co-solvent pump to gradually add a co-solvent such as water at about 0.01 to 0.1% by weight, into the dense CO<sub>2</sub> under pressure;
- a super-critical exchanger in the form of a  
5 thermostat controlled double shell;
- an extractor in the form of an autoclave with a volume of 6 litres and a maximum pressure of 300 bars provided with a double shell;
- three cyclone type separators provided with  
10 automatic pressure reduction valves.

The cork parts to be treated are placed in the autoclave and are in the form of boards or sheets with dimensions equal to a few tens of centimetres.

The cork parts to be treated are divided into two  
15 different batches:

- a first batch of cork parts was boiled in accordance with normally accepted practice for this type of material; namely immersion for 1 h 30 in water at 100°C;
- 20 - a second batch of cork parts was unboiled.

The two batches were subjected to a supplementation treatment with an aqueous solution of PCP (pentachlorophenol) and TCA (trichloroanisole) by dipping in a receptacle for several hours, namely from  
25 1 to 5 hours, with ultrasound action to complete impregnation of cork parts.

The content of PCP and TCA in the cork parts is measured before and after treatment of these parts by the process according to the invention.

30 These measurements are made by grinding the sample, liquid-solid extraction, transformation into

acetate for the PCP, purification on cartridge and analyses by gaseous phase chromatography and mass spectrometry.

Mechanical tests are also carried out on bottle  
5 corks "tubed" from treated and untreated, boiled and unboiled cork parts (boards). These tests are as follows:

- measurement of the compression pressure (PC) that consists of measuring the pressure to be applied  
10 to reduce the nominal diameter of a 24 mm bottle cork down to 16 mm, which is the compression diameter of a bottle-corking machine;

- measurement of the return pressure (Pret) that is the measurement of the pressure exerted by the  
15 bottle cork while it returns from 16 mm, which is the compression diameter of a bottle-corking machine, to 21 mm, which is the maximum diameter of a bottle neck.

Finally, microbial flora culture tests for yeast, moulds, mesophilic aerobic germs, enterobacteria,  
20 coliforms, bacillus and sulfite-reducing anaerobia, were carried out by counting on specific seeding media and evaluated by the reduction in the logarithm of the growth of this flora after treatment by CO<sub>2</sub> in the dense state under pressure, with and without water as  
25 co-solvent.

Examples 1 and 2 given below are particularly related to the elimination of organic compounds from cork samples that had previously been supplemented to make their contents very much greater than contents  
30 normally encountered in cork production intended for manufacturing bottle corks.

Example 1

Parts (boards) made of cork representing a total quantity of about 400 g of cork were treated using the process according to the invention.

5        No prior boiling treatment was done on these parts.

The initial content of PCP and TCA after an analysis using the operating method defined above, was found to be 75 ppb for each contaminating product.

10       The operating conditions of the process according to the invention are generally as follows:

- co-solvent: distilled water at about 0.2°/oo;
- operating pressures: from 100 to 300 bars;
- temperature: about 50°C;
- 15       - treatment time: from 1 to 5 hours;

At the end of this treatment, these cork parts are analysed to determine the residual content of PCP and TCA.

20       The mechanical strength of the bottle corks "tubed" from these boards is also measured by making measurements of the compression pressure "PC" and the return pressure "Pret" described above.

For the final evaluation, the measurements were also made on control bottle corks tubed in parts  
25 (boards) not treated using the process according to the invention in order to compare the mechanical strength obtained after treatment using the process according to the invention, with the strength obtained in the absence of any treatment using this process.

30       Figure 2 shows the results obtained in terms of cleaning efficiency as a percentage, which is defined

as the ratio of the contaminant masses (PCP or TCA), measured by analysis in parts before and after cleaning using the process according to the invention, and using the following formula:

5

$$\text{Efficiency \%} = \left(1 - \frac{\text{contaminant mass after treatment}}{\text{contaminant mass before treatment}}\right) \times 100$$

The cleaning efficiency is shown in figure 2 for different treatment durations and for each contaminant  
10 PCP and TCA.

Figure 3 shows the results obtained for evaluation of the mechanical strength (in N/cm<sup>2</sup>) of bottle corks  
tubed from treated and untreated cork parts (boards), using measurements of the compression pressure "PC" and  
15 the return pressure "Pret".

A control sample that was not treated using the process according to the invention is used as a reference.

Refer to table 1 for information about the results  
20 of tests on the mechanical strength of bottle corks tubed from treated and untreated cork boards using the process according to the invention.

The table also shows specific conditions for the treatment according to the invention used in this  
25 example.

#### Example 2

The process according to the invention was used to treat cork parts (boards), with a total quantity of  
30 about 400 g of product.

Unlike example 1, these parts were previously subjected to a boiling treatment (immersion for 1 h 30 in water at almost 100°C).

The initial content of PCP and TCA determined by  
5 analysis using the operating method described above, was found to be 50 ppb for each contaminating product.

The same measurements described in example 1 were made on the cork parts (boards).

These measurements were also made on bottle corks  
10 made from the control part not treated by the process according to the invention.

As in example 1, the results for the cleaning efficiency are shown in figure 2; whereas the results for the mechanical strength of bottle corks tubed from  
15 the parts (boards) are shown in figure 3 and are also given in table 1.

Table 1

Boiled boards (B)			PC (N/cm <sup>2</sup> )	Pret (N/cm <sup>2</sup> )
120 bars, 60°C, 1h, 6.5 kg/h	Test P1	Control B	26	1.8
		BP1	28	1.8
250 bars, 60°C, 5h, 10 kg/h	Test P2	Control B	26	1.8
		BP2	30	1.8
Unboiled boards (AVB)			PC (N/cm <sup>2</sup> )	Pret (N/cm <sup>2</sup> )
120 bars, 60°C, 1h, 6.5 kg/h	Test P1	Control AVB	29	1.6
		AVBP1	26	1.7
250 bars, 60°C, 5h, 10 kg/h	Test P2	Control AVB	29	1.6
		AVBP2	27	1.9

\*PC: compression pressure

Pret: return pressure

5

An analysis of the results given in examples 1 and 2 for the cleaning efficiency (figure 2), shows that the efficiency obtained after treatment according to the invention using dense CO<sub>2</sub> under pressure is very close to 100%, both for extraction of PCP for which the efficiency varies from 84 to 100%, and for extraction of TCA which is 100% in all cases.

In example 1 for unboiled samples, the efficiency ranges from 84 to 92% for extraction of PCP, which gives a residual content of 12 to 6 ppb for an initial content of 75 ppb.

The efficiency obtained for the extraction of TCA is complete and equal to 100%, which means that the

residual content of TCA is less than the detection limit of the analysis method used.

In example 2, the PCP extraction efficiency for the boiled samples is found to be slightly better and ranges from 94 to 100%, corresponding to a residual content varying from 3 ppb to a value below the detection limit of the PCP and TCA analysis method, for treatment conditions identical to those in example 1, but with a 50 ppb lower initial content of PCP and TCA.

10       The extraction efficiency on TCA is complete and equal to 100%.

For the results obtained for the mechanical strength of the bottle corks tubed from the treated cork parts (boards) (figure 3), all results in examples 15 1 and 2 show the excellent mechanical strength of cork parts treated by CO<sub>2</sub> using the process according to the invention.

A difference in the measurements of the compression pressure PC, is observed between bottle 20 corks tubed from the control parts not treated with CO<sub>2</sub> compared with bottle corks that are tubed in the parts cleaned by CO<sub>2</sub>, but this difference does not exceed 5 N/cm<sup>2</sup>.

Furthermore, the variation affecting the 25 mechanical strength is of the same order of magnitude for bottle corks tubed from treated parts as is normally obtained on bottle corks tubed from the control parts, as demonstrated by the following values of the mechanical strength:

30       - bottle corks tubed from control parts not treated with CO<sub>2</sub>;



27.5  $\pm$  1.7 N/cm<sup>2</sup> (for n = 4);

- bottle corks tubed from parts treated with CO<sub>2</sub> (examples 1 and 2);

27.8  $\pm$  1.7 N/cm<sup>2</sup> (for n = 4);

5 Similarly, no significant variation was found in the results obtained when measuring return pressures Pret, for which values obtained are:

1.7  $\pm$  0.1 N/cm<sup>2</sup> (n = 4) for control parts;

1.8  $\pm$  0.1 N/cm<sup>2</sup> (n = 4) for treated parts  
10 (examples 1 and 2).

Finally, it is observed that the density of CO<sub>2</sub> is a parameter that has less influence than the treatment time or the initial content of organic compounds responsible for the undesirable taste (PCP and TCA).

15 The results given above show that cork parts treated by the process according to the invention can also be used for stamping and / or for wine bottle corks.

### 20 Example 3

This example shows the anti-microbial efficiency of the process according to the invention when water, is added as a solvent to the dense fluid under pressure.

25 Parts of a substrate similar to the described material (cork) are thus treated by dense CO<sub>2</sub> under pressure, to which 0.02% by weight of water has been added, at a pressure of 300 bars and under a temperature varying from 0 to 60°C.

30 The growth of micro-organisms is determined using the operating method described above.

Equivalent substrate (cork) parts are treated under the same conditions, but without any water being added to the dense fluid under pressure, and the growth of micro-organisms is determined once again.

5       The results obtained are shown in figure 4 that indicates the logarithmic variation of microbial growth obtained as a function of the temperature (in °C) applied during the treatment.

10       The curve shown in solid lines is the curve for treatment by CO<sub>2</sub> to which water has been added, while the curve shown in dashed lines is applicable to treatment by CO<sub>2</sub> alone without the addition of water.

15       It is found that the treatment applied using dense CO<sub>2</sub> under pressure results in a maximum reduction in microbial growth by a factor of 100, and only for a treatment temperature of 60°C.

On the other hand, this reduction is as high as a factor of 1 million for a temperature of 40°C when CO<sub>2</sub> is used with water.

20       Without being restricted to any particular theory, it is probable that even small proportions of water in the presence of CO<sub>2</sub> produce carbonic acid such that the pH of the mix becomes acid.

25       The combined action of pressure and acidity thus produces an effect that is highly damaging to the survival of the micro-organisms present.

CLAIMS

1. Treatment process for cork or a cork-based material in which said cork or said cork-based material is put into contact with a dense fluid under pressure at a temperature of from 10 to 120°C and at a pressure  
5 of from 10 to 600 bars.

2. Process according to claim 1, in which the contact is achieved at a temperature of 40 to 80°C and at a pressure of 100 to 300 bars.  
10

3. Process according to either of claims 1 and 2, in which said dense fluid under pressure is in the super-critical state.

15 4. Process according to any one of claims 1 and 3, in which compression / decompression cycles are carried out.

20 5. Process according to claim 4, in which said compression / decompression cycles are carried out with an amplitude of the pressure variation from 10 to 100 bars and time intervals varying from 10 seconds to a few minutes, for example 10 minutes.

25 6. Process according to claim 1, in which said fluid is chosen for example from among carbon dioxide; sulphur hexafluoride; nitrous oxide; nitrogen monoxide; light alkanes for example containing 1 to 5 atoms of carbon, such as methane, propane, butane,

isobutane and pentane; alkenes, such as ethylene and propylene; and some organic liquids such as methanol and ethanol.

5           7. Process according to any one of claims 1 to 6, in which a co-solvent is added to the dense fluid under pressure.

10           8. Process according to claim 7, in which said co-solvent is chosen from among water; aqueous solutions; alcohols, for example aliphatic alcohols with 1 to 5 atoms of carbon, such as ethanol, methanol and butanol; cetones ; and mixtures thereof.

15           9. Process according to claim 8, in which said aqueous solutions are buffer solutions such as buffer solutions of phosphate and / or hydrogenophosphate; fungicide and / or antibiotic solutions such as penicillin; antioxidant solutions such as solutions of  
20 ascorbic acid.

          10. Process according to any one of claims 7 to 8 in which said co-solvent is added to the dense fluid under pressure with a content of 0.01 to 10% by weight.  
25

          11. Process according to claim 10, in which said co-solvent is added to the fluid under pressure with a content of 0.02 to 1% by weight.

30           12. Process for selective extraction of contaminating organic compounds from cork or a cork-

based material, in which said material is treated by the process according to any one of claims 7 to 11.

13. Process for selective extraction according to  
5 claim 12, in which said organic compounds are compounds responsible for undesirable tastes and/or smells.

14. Extraction process according to claim 13, in which said organic compounds responsible for the  
10 undesirable tastes and / or smells are (poly)chlorophenols and other phenolic compounds; and (poly)chloroanisoles and other derivatives of anisole.

15. Process according to claim 12, in which said  
15 organic compounds are pentachlorophenol (PCP), trichloroanisole (TCA) and tetrachloroanisole (TeCA).

16. Extraction process according to any one of claims 12 to 15, in which the dense fluid under  
20 pressure is CO<sub>2</sub> and the co-solvent is water or an aqueous solution.

17. Treatment or extraction process according to any one of claims 1 to 16, in which the fluid and the  
25 extracts are separated by one or several steps, after the treatment or the extraction by the dense fluid under pressure, and the gaseous fluid is recycled.

18. Process according to any one of claims 1 to  
30 17, in which said cork or said cork-based material is also subjected to a mechanical and / or chemical

treatment before or after said treatment or said extraction by the dense fluid under pressure, and particularly treatment by hot or boiling water commonly called a "boiling treatment".

5

19. Process according to any one of claims 1 to 18, in which said cork or said cork-based material is shaped before or after said treatment or said extraction using the dense fluid under pressure; 10 either earlier than said mechanical and / or chemical treatment, if any, preceding said treatment or said extraction by the dense fluid under pressure; or later than said mechanical and / or chemical treatment, if any, after said treatment or said extraction by the 15 dense fluid under pressure.

20

20. Process according to claim 19, in which said cork or said cork-based material is put into the form of bottle corks, boards or sheets.

25

21. Manufacturing process for bottle corks made of cork or made of a cork-base material, comprising at least one treatment or extraction step according to any one of claims 1 to 18.

30

22. Manufacturing installation for parts made of cork or of a cork-based material such as bottle corks comprising a treatment or extraction installation by bringing said cork or said material into contact with a dense fluid under pressure under the conditions specified in any one of claims 1 to 18.



ABSTRACT OF THE DISCLOSUREPROCESS FOR TREATMENT AND EXTRACTION OF ORGANIC CORK  
COMPOUNDS BY A DENSE FLUID UNDER PRESSURE

Process for the treatment of cork or a cork-based material particularly with a view towards extracting contaminating organic compounds, in which said cork or said cork-based material is put into contact with a  
5 dense fluid under pressure at a temperature of from 10 to 120°C and at a pressure of from 10 to 600 bars.

Manufacturing installation for parts made of cork or a cork-based material, such as bottle corks, comprising an installation for treatment or extraction  
10 by putting the said cork or the said material into contact with a dense fluid under pressure.

No figure.



1 / 3

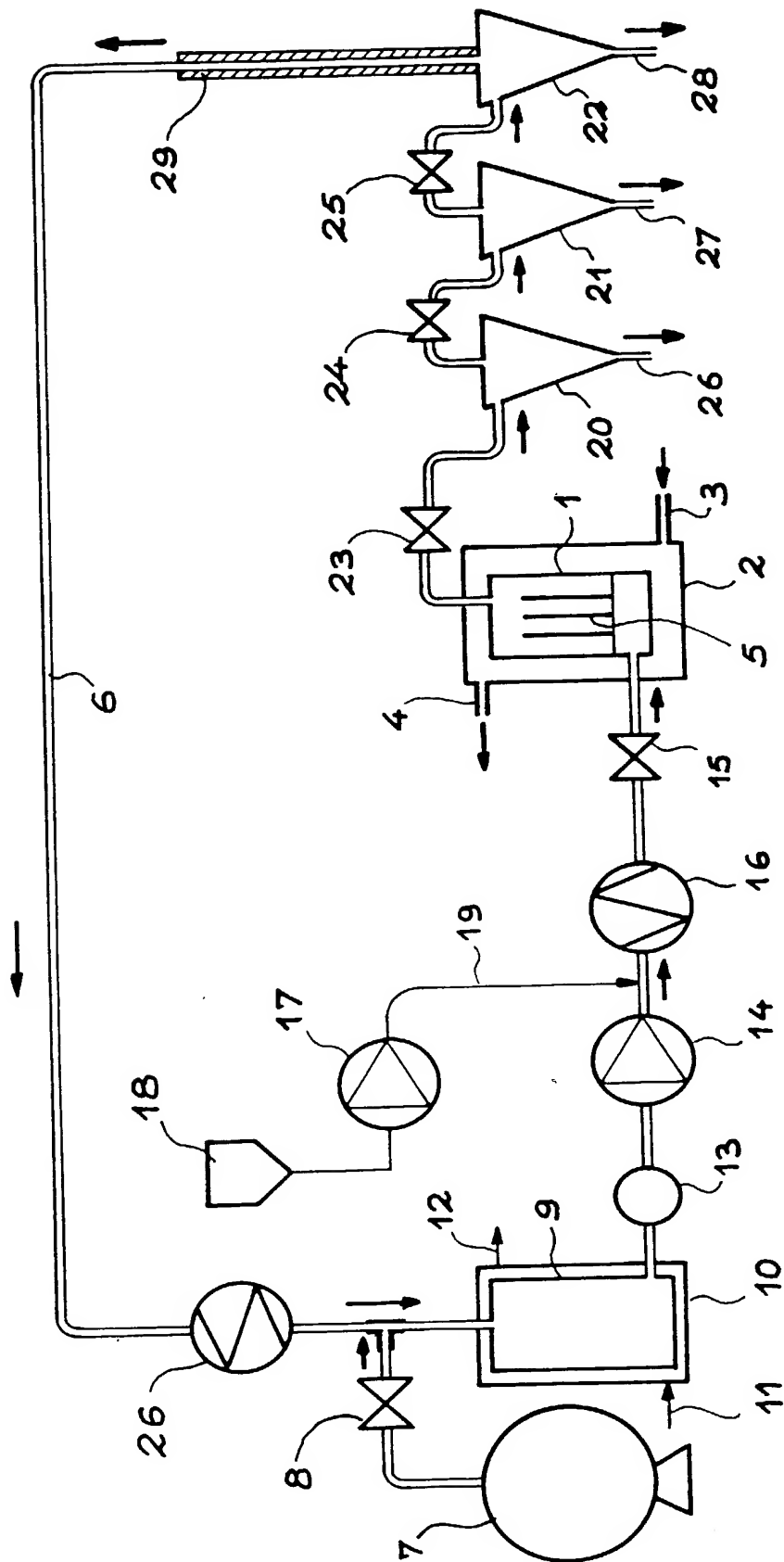


FIG. 1

2 / 3

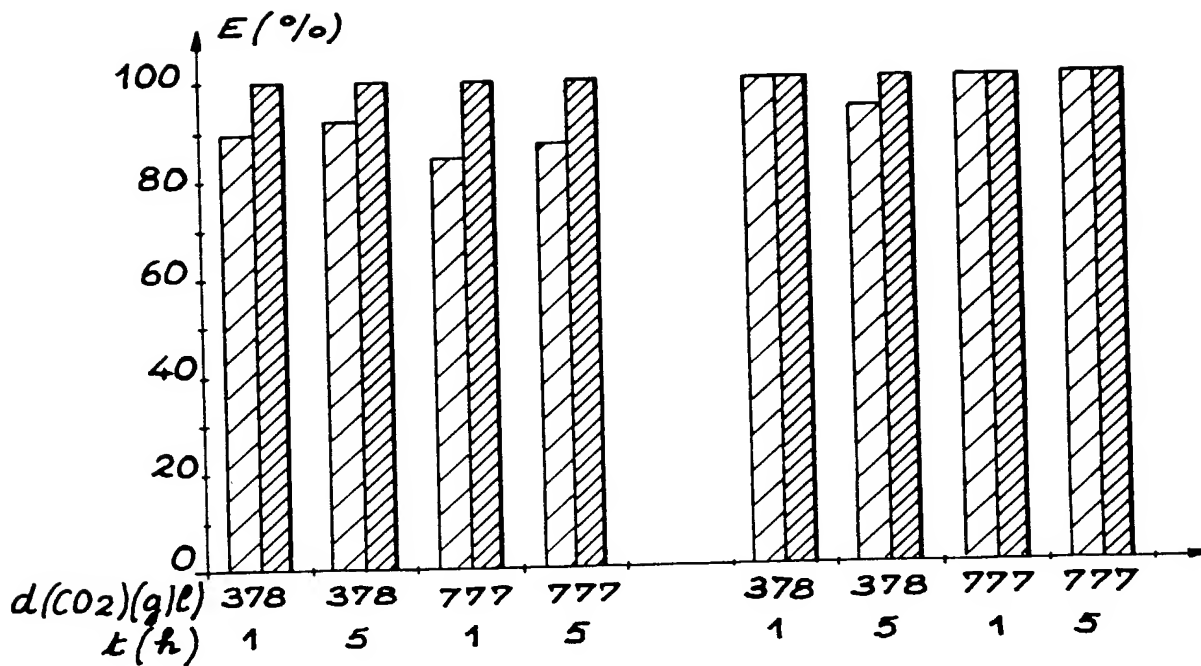


FIG. 2

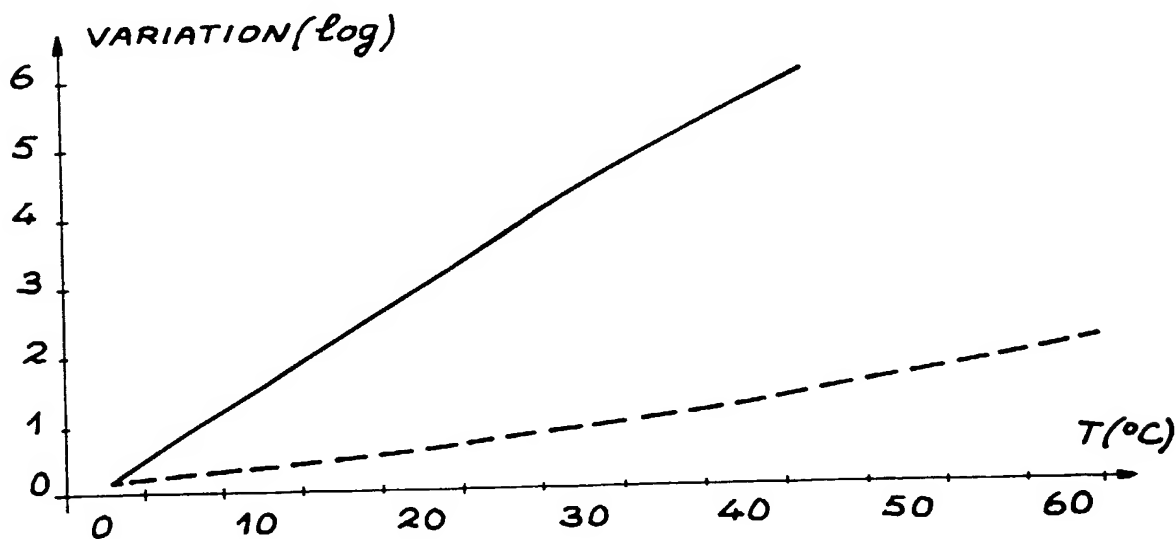


FIG. 4

3 / 3

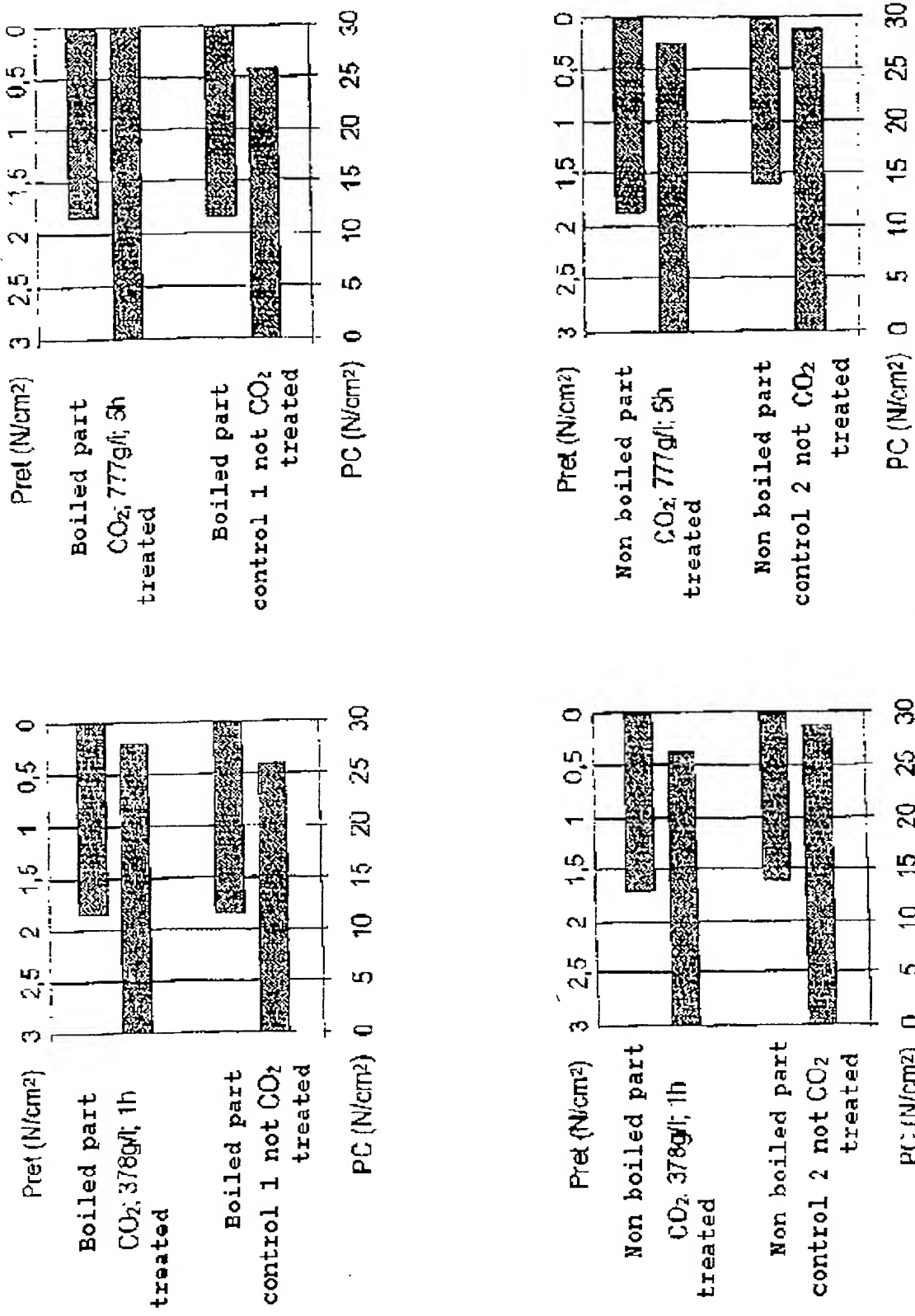


FIG. 3

**B 13335.3 PA**

### Declaration, Power Of Attorney and Petition

WE (I) the undersigned inventor(s), hereby declare(s) that :

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

## PROCESS FOR TREATMENT AND EXTRACTION OF ORGANIC CORK COMPOUNDS BY A DENSE FLUID UNDER PRESSURE

the specification of which

- ☐ is attached hereto.
- ☐ was filed on
- as Application Serial No.
- and amended on
- ☒ was filed as PCT international application
- Number PCT/FR00/02653
- on September 26, 2000
- and was amended under PCT Article 19
- on October 19, 2001

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119 (a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365 (a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application (s)

Application No.	Country	Day/month/Year	Priority Claimed	
99 12003	FRANCE	27 SEPTEMBER 1999	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO
_____	_____	_____	<input type="checkbox"/> YES	<input type="checkbox"/> NO

We (I) hereby claim the benefit under Title 35, United States Code, § 119 (c) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,  
abandoned)

And we (I) hereby appoint : Norman F. Oblon, Registration Number 24,618; Marvin J. Spivak, Registration Number 24,913; C. Irvin McClelland, Registration Number 21,124; Gregory J. Maier, Registration Number 25,599; Arthur I. Neustadt, Registration Number 24,854; Richard D. Kelly, Registration Number 27,757; James D. Hamilton, Registration Number 28,421; Eckhard H. Kuesters, Registration Number 28,870; Robert T. Pous, Registration Number 29,099; Charles L. Gholz, Registration Number 26,395; William E. Beaumont, Registration Number 30,996; Jean-Paul Lavalleye, Registration Number 31,451; Stephen G. Baxter, Registration Number 32,884; Richard L. Treanor, Registration Number 36,379; Steven P. Weihrouch, Registration Number 32,829; John T. Goolkasian, Registration Number 26,142; Richard L. Chinn, Registration Number 34,305; Steven E. Lipman, Registration Number 30,011; Carl E. Schlier, Registration Number 34,426; James J. Kulbaski, Registration Number 34,648; Richard A. Neifeld, Registration Number 35,299; J. Derek Mason, Registration Number 35,270; Surinder Sachar, Registration Number 34,423; Christina M. Gadiano, Registration Number 37,628; Jeffrey B. McIntyre, Registration Number 36,867; William T. Enos, Registration Number 33,128; Michael E. McKabe Jr., Registration Number 37,182; Bradley D. Lytle, Registration Number 40,073; and Michael R. Casey, Registration Number 40,294; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., whose post Office Address is : Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardise the validity of the application or any patent issuing thereon.

LUMIA Guy

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Signature of Inventor

March 13, 2002

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Signature of Inventor

March 13, 2002  
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NAME OF FOURTH INVENTOR

Signature of Inventor

Date

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